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ADP012198

TITLE: In-Situ Analysis of the Chemical Vapor Synthesis of Nanocrystalline Silicon Carbide by Aerosol Mass Spectrometry

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In-situ Analysis of the Chemical Vapor Synthesis of Nanocrystalline Silicon Carbide by Aerosol Mass Spectrometry

In-Kyum Lee, Markus Winterer, Horst Hahn, Christian Janzen[1], Dirk Lindackers[1], Paul Roth[1]
Darmstadt University of Technology, Institute of Materials Science,
Petersenstr. 23, 64287 Darmstadt, Germany
[1]Institut of Combustion and Gasdynamics, Gerhard-Mercator University,
47048 Duisburg, Germany

Abstract

An Aerosol Mass Spectrometer (AMS) is a combination of a Quadrupol- (QMS) and a Particle Mass Spectrometer (PMS) and enables the in-situ analysis of gas phase processes for the generation of nanoparticles. Size distributions of ultrafine silicon carbide particles in the range of 10^4 atomic mass units (amu) to 10^7 amu are measured in the PMS. Simultaneously, molecular species up to 300 amu can be detected in the QMS. Aerosols containing nanocrystalline silicon carbide are produced from tetramethylsilane (TMS) by thermal decomposition. In situ process analysis with the AMS as a function of process parameters was performed to elucidate the formation and growth mechanism of SiC nanoparticles.

1. Introduction

Powders of small grain size, narrow size distribution, low agglomeration and high purity are required for the production of solid nanocrystalline materials and the exploitation of size effects in applications (Winterer 2001 and multiple references therein). The synthesis of particles from the gas phase is one important technique to produce ultrafine particles with a narrow size distribution and high purity. Chemical Vapor Synthesis (CVS) is a method to generate particles in the size range below 10 nm, narrow size distribution, geometric standard deviation smaller than 1.2 and low degree of agglomeration. Silicon Carbide is an advanced ceramic material for high performance applications. Sintering of SiC to high density is very difficult because of low diffusion coefficient even at high temperatures due to strong covalent bonds. Ultrafine particles of SiC are promising for the production of dense bulk solids due to the small grain size of such powders. Up to now, CVS powders have been analysed only by ex situ methods (Klein 1998). In situ analysis methods of CVS processes have to be compatible with high temperatures, low pressures, high particle number concentration and very small particle size of the order of a few nanometers. One instrument which meets those requirements is called AMS, which has been used for particle size measurements in premixed low pressure flames (Roth 1993, Homann 1987).

2. Methodology

Chemical Vapor Synthesis

In the Chemical Vapor Synthesis (CVS) process a precursor vapor with carrier gas is delivered into a hot wall reactor. The precursor is thermally decomposed and particles form by coagulation and sintering. Process parameters like temperature, pressure, mass flow, precursor concentration, precursor material and reactor geometry influence the time-temperature history of the particles and determine the particle size and chemical purity of the powder. For the synthesis of SiC the precursor, TMS, is evaporated at room temperature and is directly delivered through a thermal mass flow controller into the reactor. To adjust residence time and precursor concentration an additional helium flow is used. The mass flow of helium is controlled by a second thermal mass flow controller. The total, absolute pressure is measured with a Baratron capacitance gauge. The continuous gas flow is produced by a combination of a roots blower and a sliding vane pump and stabilised at different pressures by means of a butterfly valve (figure1).
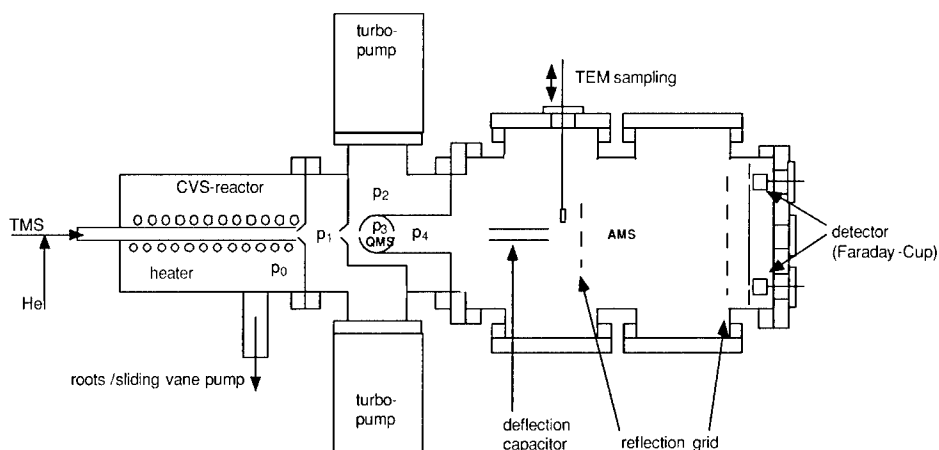
Figure 1. CVS reactor attached to the Aerosol Mass Spectrometer for in situ process analysis.

Aerosol Mass Spectrometer

A new Aerosol Mass Spectrometer (AMS) was constructed by combining a Quadrupol Mass Spectrometer (QMS) (Balzers, QMA 430 with QMG 422) and a Particle Mass Spectrometer (PMS) (Roth 1993) (figure 1). Molecular species in the mass range 0-300 atomar mass units (amu) can be measured in the QMA. Particulate Species in the mass range 10^4 to 10^7 amu, corresponding to a diameter of 1 to 35 nm for SiC, can be measured in the PMS. The aerosol from the reaction chamber, which is in the continuous pressure regime (p_0) is supersonically expanded through a nozzle (0.8 mm diameter) into the first vacuum chamber (p_1, figure 1). Due to the high pressure ratio larger than 10^4 a molecular free jet is generated, where all reactions, coagulation and sintering processes are quenched. The pressure in the first vacuum chamber is smaller than 10^{-3} mbar and pumped by a 1000 l/s turbomolecular pump (Pfeiffer Vakuum TMP 1001 SG). The center of the molecular free jet is extracted by a sharp edged skimmer (Molecular Beam Dynamics Standard Model 1, with 0.5mm orifice diameter) to generate a molecular beam (p_2, figure 1). The molecular beam (aerosol) is ionised in a cross beam ion source, which is part of the QMA, by electron impact (p_3, figure 1). Molecular species up to a mass of 300 amu can be analysed in the QMA. The separation of the particles is realised by their electrical charge and their inertia. A detailed description of the fundamentals of the PMS is given in (Roth 1993). The molecular beam enters a homogeneous electrical field, which is perpendicular to the molecular beam direction. The electrical field is realised by a capacitor with 100 mm in length and a distance of 20 mm. Charged particles are accelerated in the electrical field in direction of the field lines. Outside the electrical field the particles move in a straight line. For fixed geometric conditions of the detector the voltage U_k selects particles of a certain kinetic energy carrying z elementary charges. By varying the voltage and therefore the electrical field of the capacitor a signal $I(U_k)$ is detected.

$$U_k = \text{const.} \; \frac{m_p}{ze} \frac{v_p^2}{2} \tag{1}$$

where U_k is the deflection voltage, m_p the particle mass, v_p the particle velocity, e the elementary charge, z the number of charges and I is the current measured by the ion detectors of the Faraday cup. With the information of the kinetic energy of the particles mass distributions can be determined if the particle velocity is known. The particle velocity is measured in an electrical

chopping system with a synchronously pulsed repelling potential. By sweeping the chopping frequency of the repelling potential a periodic signal is measured. The determination of the particle velocity is then given by the following equation:

$$v_p = \Delta f_{min} (I_{min}) \, l_{rg} \tag{2}$$

where v_p is the particle velocity, $\Delta f_{min} (I_{min})$ the frequency of the signal at minimum signal intensity, and l_{rp} the distance of the reflection grids. Figure 3 and 4 show a typical measurement.

3. Results and Discussion

Detection of the Molecular Species (QMA):

The thermal decomposition of TMS in the CVS reactor was measured using the QMS at different temperatures of the hot wall reactor at otherwise constant process parameters (2000 Pa, 800 sccm He and 30 sccm TMS; sccm stands for standard cubic centimeter). The decomposition of the TMS precursor (m/e = 73) starts at about 1173K and the signal vanishes at about 1673 K where the precursor is completely decomposed (figure 2). With increasing temperature an increase of lower hydrocarbon groups and also an increase of carbon and hydrogen is observed. Also observed is the occurrence of species of masses higher than 88 amu at the beginning of the precursor decomposition. This indicates that formation of nano SiC takes place by a polymerisation reaction as discussed by Fritz (Fritz 1986). With increasing temperature the signal of the higher masses decreases. It is not clear if species of higher masses decompose with increasing temperature or whether the polymerisation reaction goes on to form nano SiC. A signal in the PMS is observed as soon as a decrease of the TMS signal is measured in the QMS. Therefore, at 1173 K TMS is decomposed and converted to SiC particles. The intensity of this signal increases from 1173 K to 1473 K.
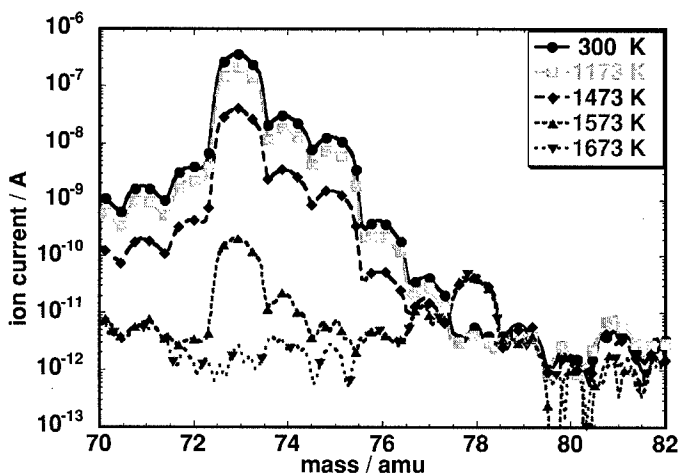

Figure 2. Quadrupol mass spectrum of the tetramethylsilane base peak (m/e 73 at 70 eV) at different temperatures.

Detection of the Particular Species (PMS):

In the following plots the classification by the deflection voltage and the velocity determined at the maximum intensity of the deflection voltage are shown. The synthesis conditions were as follows: T = 1323 K, p = 2000 Pa, 800 sccm He flow and 30 sccm TMS flow. It was found that particle charging by an external ion source is not necessary. The SiC particles are charged bipolarly in the CVS process as detected by switching the polarity of the deflection voltage. The maximum intensity at the kinetic energy filter is measured at 130 V. A velocity of 530 m/s was detected. The particle size distribution calculated from these data is shown in figure 5.
The distribution is fitted by a lognormal function and a particle mean diameter of approximately 13.5 nm with a geometric standard deviation of about 1.1 is deducted.
This PMS size distribution is compared with a TEM sample, which was taken directly from the molecular beam (figure 5). Altough only approximately 120 particles were measured by TEM the size distribution (histogram) shows a good agreement with the PMS data. In contrast the measured ion current in the PMS (figure 3) is about 4 pA at the maximum, which corresponds to about 10^7 single charged particles. The size distribution from the TEM data was also fitted by a lognormal function and gives a mean particle diameter of 15.7 nm with a geometric standard deviation of 1.3. Measurements with increasing He flow (800/1200/1500 sccm) but otherwise constant process conditions, i.e.shorter residence time result in a decrease of particle diameter (14.9, 10.8, 8.9 nm ($\pm$ 0.5 nm)). These trends are also predicted by a monodisperse reaction coagulation sintering model (Winterer, 2001).
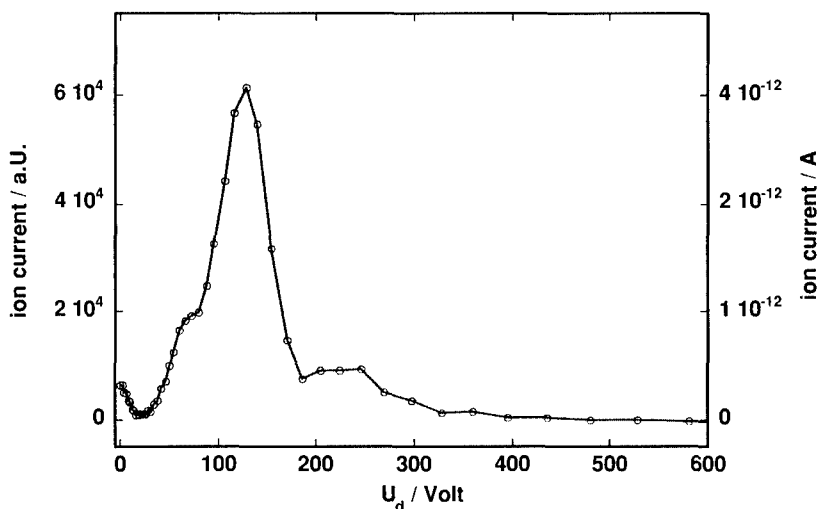
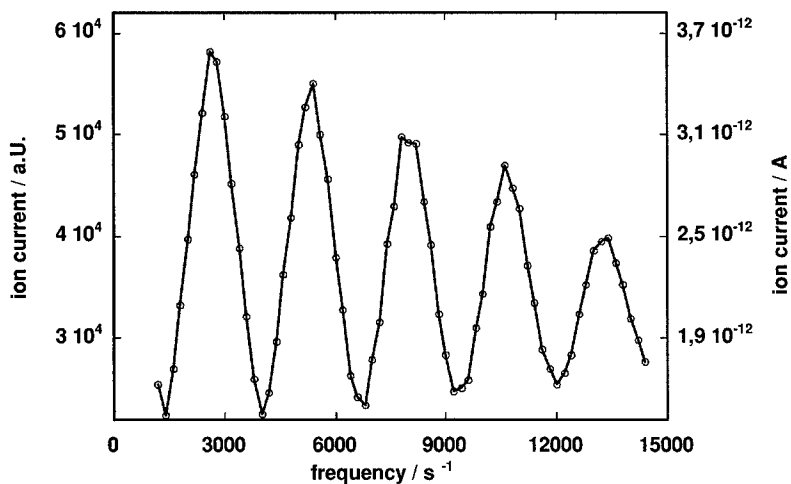

Figure 3. Measured kinetic energy distribution

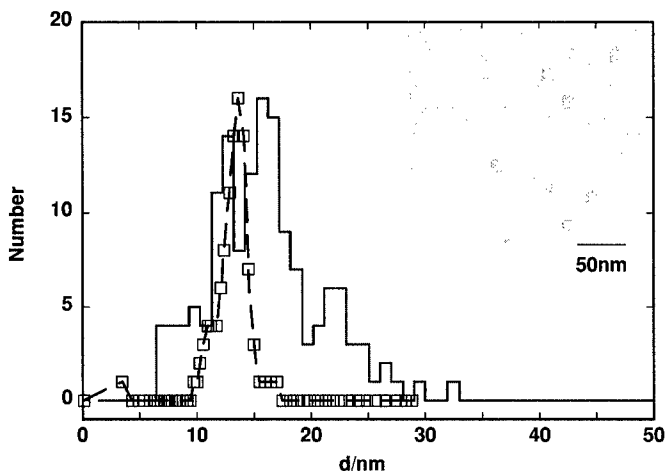**Figure 4.** Measured particle velocity.

Figure 5. Particle size distribution from PMS measurements (squares) compared with TEM sampling (full line).

4. Conclusions

The AMS allows the in situ analysis of high temperature, low pressure gas phase processes. Particular and molecular type species can be detected simultaneously allowing the optimisation of the particle size distribution and the determination of precursor decomposition kinetics. The synthesis of nano SiC by thermal decomposition of TMS has been analysed. At about 1173 K the beginning of TMS decomposition is observed. At this point particles are detected in the PMS. Particle sizes between 1-35 nm of SiC can be measured in the PMS with an accuracy of about 8 % in size or 25 % in mass in the measured range. To simulate CVS processes with particle size distributions models without restriction to monodispersity have to be used, e.g. a sectional model (Landgrebe 1990).

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